

## Dry Deposition Monitoring Protocol

Monitoring Atmospheric Pollutants in Dry Deposition



Petrified Forest National Park, AZ

Air Resources Division Research and Monitoring Branch Lakewood, CO

May 2006

# Dry Deposition Monitoring Protocol

### Monitoring Atmospheric Pollutants in Dry Deposition

Air Resources Division, National Park Service WASO-ARD P.O. Box 25287 Denver, CO 80225-0287

National Park Service U.S. Department of the Interior Washington, D.C.

**D-1770/May 2006** 

Prepared by Ellen Porter, Air Resources Division (ellen\_porter@nps.gov)

#### **FOREWORD**

This document is intended to provide guidance to natural resource managers who are considering including dry atmospheric deposition monitoring in their Vital Signs monitoring strategy. The information will help managers decide if dry deposition monitoring would help a park or network meet resource management objectives, and presents appropriate monitoring methods. The types of data provided by monitoring and requirements for monitor siting, operation, data handling, and costs are discussed and referenced. Parks are strongly urged to contact the National Park Service, Air Resources Division for additional guidance on dry deposition monitoring.

Additional protocols are available for wet atmospheric deposition monitoring and wet atmospheric mercury deposition monitoring at <a href="http://www2.nature.nps.gov/air/permits/aris/networks/index.cfm">http://www2.nature.nps.gov/air/permits/aris/networks/index.cfm</a>.

For further information, please contact:

Kristi Morris
Deposition Monitoring Program Manager
Air Resources Division, National Park Service
(303) 987-6941

kristi\_morris@nps.gov

or

Dr. John Ray
Gaseous Pollutant Monitoring Program Manager
NPS Air Resources Division
(303) 969-2820
john\_d\_ray@nps.gov

This document is also available at <a href="http://www2.nature.nps.gov/air/Monitoring/docs/200605FinalDryDepProtocol.pdf">http://www2.nature.nps.gov/air/Monitoring/docs/200605FinalDryDepProtocol.pdf</a>

#### 1.0 OVERVIEW

#### 1.1 BACKGROUND

Atmospheric deposition is the process by which airborne particles and gases are deposited to soils, vegetation, waters, and other surfaces, either through precipitation (rain, snow, clouds, and fog) or as a result of complex atmospheric processes such as settling, impaction, and adsorption, known as dry deposition. Wet or dry deposition of nitrogen and sulfur compounds can result in acidification of freshwaters, loss of aquatic species, eutrophication of estuarine and near-coastal waterways, soil nutrient and base cation leaching, and vegetation changes.

The National Park Service (NPS) is responsible for the protection and conservation of the areas it manages in order to "leave them unimpaired for the enjoyment of future generations" (Organic Act of 1916). NPS also has an affirmative responsibility under the Clean Air Act to protect parks and their resources from sources of air pollution and to participate in national and regional initiatives to control air pollution. Protecting resources in our national parks from the effects of atmospheric deposition requires extensive knowledge about the origin, transport, and transformation, and effects of deposition.

Since the late 1970s, the NPS Air Resources Division (ARD) has managed a comprehensive air quality program, emphasizing the collection of credible air quality information to support scientifically sound resource management decisions in parks. In general, air quality monitoring in parks is done in conjunction with national networks for deposition, ozone, and visibility (<a href="http://www2.nature.nps.gov/air/monitoring/index.cfm">http://www2.nature.nps.gov/air/monitoring/index.cfm</a>). This cooperative approach has been successful in producing high quality, defensible data that is spatially and temporally comparable, and provides a broad context for an individual park's air quality information. It is strongly recommended that resource managers considering long-term air quality monitoring adopt this cooperative approach, because partnerships with national monitoring networks use limited funding more effectively and provide a more complete database on which to base air quality management decisions. In addition, monitoring and research activities by agency and university scientists should be encouraged to gain a better understanding of ecosystems and how they might be affected by air pollution.

Dry atmospheric deposition of pollutants is monitored at approximately 80 sites nationwide (March 2006) as part of EPA's Clean Air Status and Trends Network (CASTNet). The CASTNet website (<a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>) contains information on the network and provides data access. Twenty-seven CASTNet sites are in national parks (Figure 1-1). NPS AirWeb provides further information on CASTNet sites on NPS lands at <a href="http://www2.nature.nps.gov/air/monitoring/drymon.cfm">http://www2.nature.nps.gov/air/monitoring/drymon.cfm</a>. CASTNet sites include meteorological measurements; most also include continuous ozone measurements. CASTNet has evolved from the National Dry Deposition Network (NDDN), which began operation in 1987.

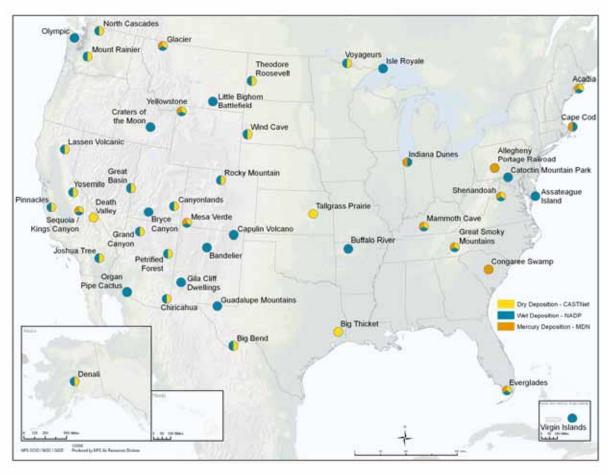


Figure 1-1. NPS monitoring sites for wet, dry, and wet mercury deposition. (May 2006)

Total deposition is commonly calculated by adding dry and wet deposition as measured by CASTNet and the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). NADP/NTN measures pollutants in rain and snow; their website (<a href="http://nadp.sws.uiuc.edu/">http://nadp.sws.uiuc.edu/</a>) contains information on the network and provides data access. A wet deposition monitoring protocol for parks is available at <a href="http://www2.nature.nps.gov/air/permits/aris/networks/index.cfm">http://www2.nature.nps.gov/air/permits/aris/networks/index.cfm</a>. CASTNet and NADP/NTN samplers may underestimate deposition in areas of high snowfall, clouds, or fog. Methods of measuring deposition from clouds, fog, and snow are not widely standardized in national networks and have been done primarily on a site- or region-specific basis using techniques such as snowpit sampling, throughfall samplers, and cloud/fog collectors.

Figures 1-2 and 1-3 show the spatial distribution of sulfur and nitrogen deposition. Deposition of both sulfur and nitrogen is generally higher in the East, due to greater population and greater emissions in the East. The east-west gradient for sulfur deposition is quite pronounced, due to the fact that sulfur deposition comes primarily from sulfur dioxide emissions from coal-burning power plants in the East (however, many new coal-burning power plants are being planned for the West). Nitrogen deposition comes from more evenly distributed sources, like automobiles and agricultural activities. The maps also illustrate that, for most areas, wet deposition comprises more than 50 percent of sulfur and nitrogen total deposition.

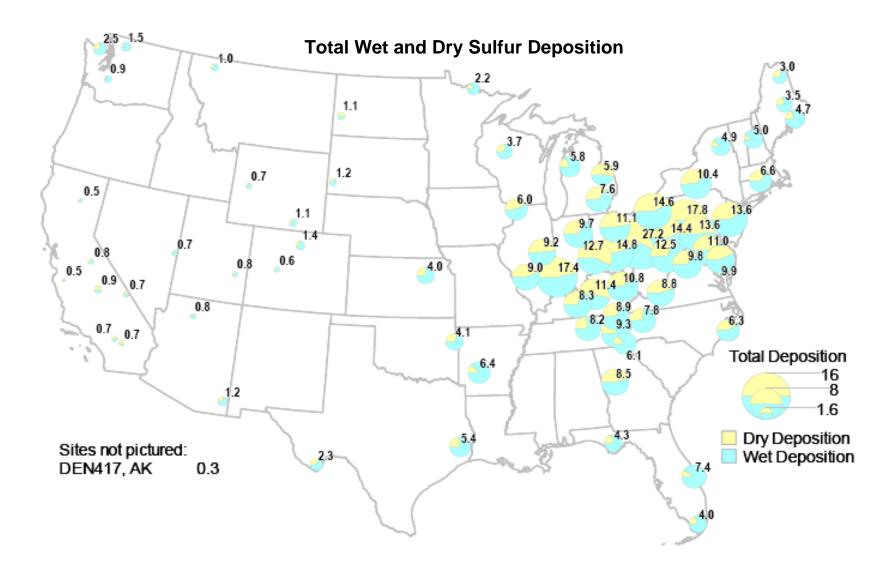


Figure 1-2. Scaled pie charts depict the 2004 total **sulfur** deposition in kilograms per hectare at CASTNet sites. Wet deposition data (blue) are from NADP measurements. Dry deposition data (yellow) are from CASTNet measurements. Total deposition is indicated in or next to each chart (from CASTNet 2004 Annual Report at <a href="http://www.epa.gov/castnet/library.html">http://www.epa.gov/castnet/library.html</a>).

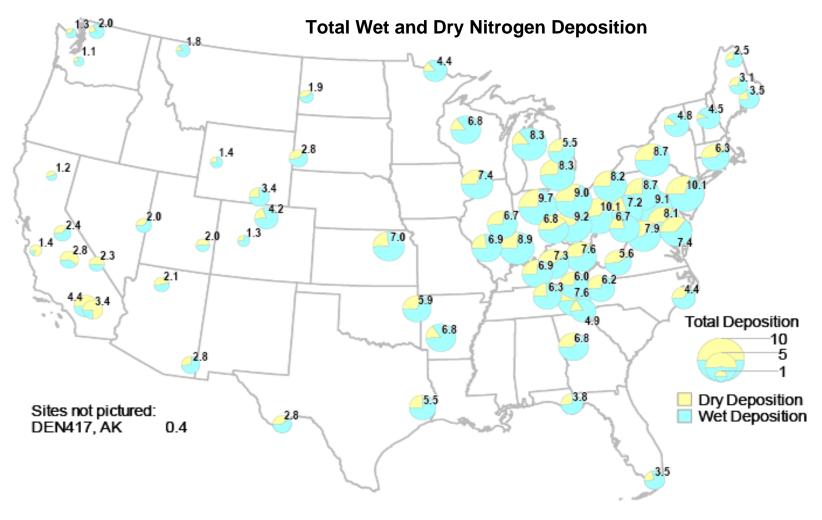


Figure 1-3. Scaled pie charts depict the 2004 total **nitrogen** deposition in kilograms per hectare at CASTNet sites. Wet deposition data (blue) are from NADP measurements. Dry deposition data (yellow) are from CASTNet measurements. Total deposition is indicated in or next to each chart (from CASTNet 2004 Annual Report at <a href="http://www.epa.gov/castnet/library.html">http://www.epa.gov/castnet/library.html</a>).

### 1.2 EFFECTS OF ATMOSPHERIC DEPOSITION OF NITROGEN AND SULFUR COMPOUNDS

CASTNet analyzes filter pack samples for a number of cations and anions. Nitrogen and sulfur compounds are the most ecologically significant compounds analyzed by CASTNet; nitrogen and sulfur are emitted by a variety of both anthropogenic and natural sources, including automobiles, power plants, industries, agriculture, and fires. Nitrogen and sulfur deposition affects freshwater lakes, streams, and soils. These effects include changes in water chemistry (acidification) that affect algae, fish, submerged vegetation, and amphibian and aquatic invertebrate communities. These changes can result in higher food chain impacts in park ecosystems. Deposition can also cause chemical changes in soils that affect soil microorganisms, plants, and trees. In addition to acidification effects, nitrogen compounds may cause fertilization or eutrophication. Nitrogen fertilization of natural ecosystems is generally unwanted and can favor certain species of plants over others, altering plant communities and facilitating invasion of non-native species. Excess nitrogen also contributes to nutrient enrichment in coastal and estuarine ecosystems, the symptoms of which include toxic algal blooms, fish kills, and loss of plant and animal diversity.

High elevation ecosystems in the Rocky Mountains, Cascades, Sierra Nevada, southern California, and the upland areas of the eastern U.S. are generally the most sensitive to atmospheric deposition due to their poor ability to neutralize acid deposition. Other sensitive areas include the upper Midwest, New England, and Florida, including the shallow bays and estuaries along the Atlantic and Gulf Coasts. Streams in both Shenandoah and Great Smoky Mountains National Parks are experiencing chronic and episodic acidification and brook trout fisheries in Shenandoah have been affected. Rocky Mountain National Park is also currently undergoing subtle changes in aquatic and terrestrial ecosystems attributable to atmospheric deposition.

#### 1.3 MEASUREABLE OBJECTIVES

Atmospheric deposition of nitrogen and sulfur is not regulated under the Clean Air Act. However, data from CASTNet and NADP/NTN are used by the Environmental Protection Agency to assess progress in achieving emissions reductions of nitrogen oxides and sulfur dioxide under the Act. NPS-ARD also uses dry deposition in combination with wet deposition estimates to evaluate total (wet plus dry) deposition loadings to ecosystems. NPS-ARD is currently (2006) developing strategies for quantifying the amount of deposition that would be harmful for specific sensitive resources in parks. This amount is termed the "critical load," that is, the amount of deposition of a given pollutant below which significant harmful effects to sensitive resources do not occur. A target load is often used in conjunction with a critical load. A target load is the deposition of air pollution that will result in an acceptable level of

resource protection, taking into account political, economic, or temporal considerations. NPS would select target loads that were lower than critical loads, to provide a conservative level of protection. Long-term deposition monitoring may enable managers to evaluate whether total deposition is below or above critical or target loads.

## 1.4 DEPOSITION MONITORING AND RESOURCE MANAGEMENT OBJECTIVES

Resource managers may want to initiate on-site dry deposition monitoring to assess risks to sensitive lakes, streams, soils and vegetation within their park unit. Managers should first consider whether representative monitoring data are available. Figure 1-1 and maps available on the CASTNet web site (<a href="http://www.epa.gov/castnet/mapindex.html">http://www.epa.gov/castnet/mapindex.html</a>) will help identify existing monitors. NPS has dry deposition samplers in 27 parks that are part of a CASTNet network of over 80 sites. The majority of parks, however, have no on-site or nearby dry deposition monitoring. A rough estimate of total deposition for these parks can be made by doubling the wet deposition values; as noted above and illustrated by Figures 1-2 and 1-3. Wet deposition at most sites is at least 50 percent of total deposition, therefore doubling wet deposition to calculate total deposition provides a conservative estimate. However, for individual CASTNet sites (particularly sites in southern California), dry deposition of either sulfur or nitrogen can be as high as 80 percent of total deposition. For these sites, doubling wet deposition would result in a gross underestimate. Sulfur and nitrogen wet deposition estimates for all parks are available from NPS Air Atlas

(http://www2.nature.nps.gov/air/Maps/AirAtlas/index.cfm).

#### 2.0 DRY DEPOSITION MONITORING

The national network for monitoring dry atmospheric deposition is CASTNet. It is strongly recommended that dry deposition monitoring in parks be done in partnership with CASTNet in order to use limited funding more effectively and contribute to a more complete database on which to base air quality management decisions. Other deposition measurement methods, including throughfall methods, are now being used as part of special studies in some areas to estimate deposition; however, CASTNet provides a national framework for standardized dry deposition measurements.

Information on CASTNet is at <a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>. This web site contains site information and data, annual reports, quality assurance reports and standard operating procedures (SOPs). SOPs are described in detail in the CASTNet Quality Assurance Project Plan at <a href="http://www.epa.gov/castnet/library/qapp\_v2.html">http://www.epa.gov/castnet/library/qapp\_v2.html</a>. This document has field, laboratory, data operations, and other SOPs, as well as a Quality Management Plan. At CASTNet sites, fine particles and gases suspended in the air are collected over a week-long period on a sequence of filters (Figure 2-1). The filters are analyzed at a central laboratory for concentrations of sulfur dioxide, sulfate, nitrate, nitric acid, and ammonium in the air sample; concentrations are expressed in micrograms per cubic meter

 $(\mu g/m^3)$ . It is important to note that CASTNet does not collect all the chemical species in the atmosphere that contribute to nitrogen or sulfur deposition. For example, CASTNet does not measure gaseous ammonia; gaseous ammonia can directly deposit near its source or be transformed in the atmosphere to particulate ammonium, which is measured by CASTNet. At present, there is no national monitoring network for gaseous ammonia, although it is a significant contributor to total nitrogen deposition.

Meteorological, vegetation, and land use data from the site are used as input to the Multi-Layer Model (MLM), a mathematical model that simulates atmospheric dry deposition processes (Figure 2-2). The MLM is used to calculate deposition velocities, which are combined with the concentration measurements to estimate dry deposition of gaseous and particulate pollutants. There are varying degrees of uncertainty in the deposition velocities, due to site-specific differences and complexities in vegetation and meteorology. Dry deposition is expressed in kilograms per hectare per year (kg/ha/yr).



Figure 2-1. CASTNet Filter Pack (CASTNet 2004 Annual Report)

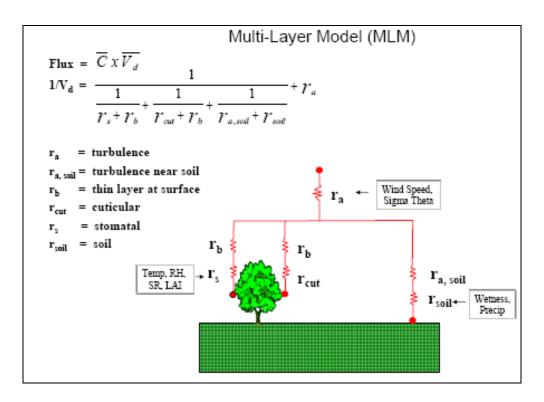


Figure 2-2. Multi-layer model. Dry deposition is the product of pollutant concentration (C, from filters) and modeled deposition velocity ( $V_d$ ). Deposition velocity is modeled as resistances to deposition, considering temperature (Temp), relative humidity (RH), solar radiation (SR), and LAI (leaf area index) (CASTNet 2004 Annual Report).

#### Site Selection and Site Operation

The CASTNet Quality Assurance Project Plan, Section B, discusses site selection, operator training, site operation, laboratory analysis, and other aspects of project operations (<a href="http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf">http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf</a>). In general, a site should be located at some distance from sources of air pollution; data collected at the site should represent regional conditions. Table 2-1 lists some siting requirements.

Table 2-1. Site-specific siting criteria for CASTNet monitoring sites (http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf, Table 2.B.1).

Potential Interferant	Minimum Distance From Measurement Apparatus
Large point source of SO <sub>2</sub> or NO <sub>x</sub>	20 to 40 km
Major industrial complex	10 to 20 km
City, > 50,000 population	40 km
City, 10,000 to 50,000 population	10 km
City, 1,000 to 10,000 population	5 km
Major highway, airport, or rail yard	2 km
Secondary road, heavily traveled	500 m
Secondary road, lightly traveled	200 m
Feedlot operations	500 m
Intensive agricultural operations (including aerial spraying)	500 m
Limited agricultural operations	200 m
Large parking lot	200 m
Small parking lot	100 m
Tree line	50 m
Obstacles to wind	10 times obstacle height

#### 2.2 FIELD METHODS

Site operations are described in detail in the CASTNet Quality Assurance Project Plan, Section B (<a href="http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf">http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf</a>). In brief, ambient air is pumped through the filter packs for a one-week period. Every Tuesday morning, the site operator replaces the exposed filter pack and ships it to the central analytical laboratory. The site operator also evaluates equipment status and performance and performs preventative maintenance. Supporting paperwork is completed and site operators participate in Tuesday telephone calls with the Field Operations Manager. Site operators record surface conditions (e.g., dew, frost, snow) and vegetation status weekly; vegetation status and land-use information are archived and used to define the distribution and condition of plant species around each site that could influence deposition rates for gases and particles.

#### 2.3 DATA HANDLING AND ANALYSIS

Data management and validation are described in the CASTNet Quality Assurance Project Plan, Sections B and D (<a href="http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf">http://www.epa.gov/castnet/library/qapp\_v2/qapp\_a-f.pdf</a>). Data are available from the CASTNet website at <a href="http://cfpub.epa.gov/gdm/index.cfm?fuseaction=aciddeposition.wizard">http://cfpub.epa.gov/gdm/index.cfm?fuseaction=aciddeposition.wizard</a>. Both concentration and deposition data are available, as well as charts and graphs.

#### 2.4 MONITORING COSTS

Approximate monitoring costs are given in Table 2-2. In general, CASTNet dry deposition monitoring equipment is co-located with an ozone monitor. Cost savings would be realized if the CASTNet dry deposition equipment were placed at an existing air quality monitoring site with an existing shelter, computer, datalogger, and utilities.

Table 2-2. March 2006 Monitoring Costs for Dry Deposition CASTNet Monitoring\*

		Costs*
Initial/Start-up		
Equipment	<ul> <li>CASTNet filter pack flow system (filter pack, tipping tower, plumbing, flow box with mass flow controller)</li> </ul>	\$10,500
	<ul> <li>Meteorological equipment (sensors for wind direction and speed, air temperature, temperature gradient, relative humidity, solar radiation, precipitation, leaf wetness, barometric pressure; lighting protection and surge protection provided on a 10-m pole hinged tower)</li> </ul>	\$12,800*
	Datalogger	\$7,800*
	<ul> <li>Data-View site management system (computer)</li> </ul>	\$3,600*
	• Shelter – climate controlled	\$16,500* (varies)
	<ul> <li>Utilities (phone/power/access)</li> </ul>	\$3,300*(varies)
Installation, site preparation, operator training	u i	\$18,700* (varies)
g	Initial/Start-up Total Costs	\$73,200 (varies)
Operation (cost/yr)	• Filter pack analysis: Analytical laboratory services, semi- annual calibration and maintenance, data collection, validation, and reporting	\$11,000
	<ul> <li>Meteorological data collection, validation, reporting, and twice-annual maintenance and calibration</li> </ul>	\$11,000*
	Data-View/computer maintenance	\$2,750*
	Annual Costs Total	\$24,750

First year costs (start-up plus operating costs): \$97,950

Subsequent year costs: \$24,750

#### 3.0 DATA REPORTING

The following section describes options for reporting dry deposition data. Several data products are produced by CASTNet and are available on their website, including national maps, pie charts of dry deposition components, and bar charts showing temporal trends.

<sup>\*</sup>Costs assume that no other equipment exists at site; however, CASTNet dry deposition samplers are usually co-located with ozone analyzers. A site with an existing ozone analyzer might already have the equipment marked by an \*; therefore costs for adding a dry deposition sampler would be greatly reduced.

CASTNet also displays wet deposition data from NADP in order to present total deposition. The following pie charts (Figure 3-1) from CASTNet show that wet deposition (nitrate and wet ammonium in rainfall) contributes about 60 percent to total N deposition at Shenandoah NP (SHN418); dry deposition (nitrate, nitric acid, and ammonium) contributes about 40 percent to total N deposition at the park. The proportions are similar for wet and dry S deposition (from wet sulfate, dry sulfate and sulfur dioxide).

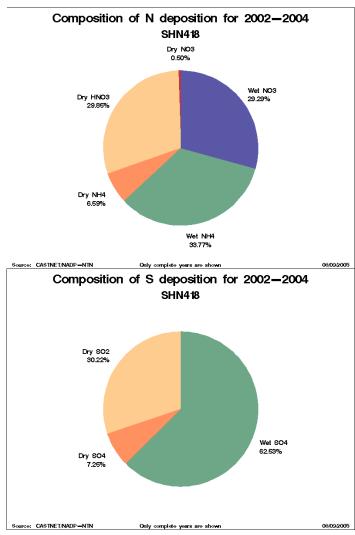


Figure 3-1. Example pie charts showing composition of total nitrogen and sulfur deposition by species in Shenandoah NP (from CASTNet at <a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>); NO3=nitrate; HNO3=nitric acid; NH4=ammonium; SO2=sulfur dioxide; SO4=sulfate.

The following bar charts (Figure 3-2) show trends in wet and dry deposition at Shenandoah NP. Both nitrogen and sulfur appear to be decreasing at the park.

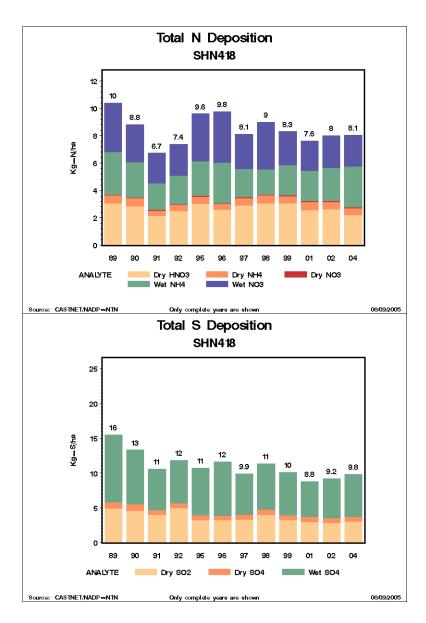
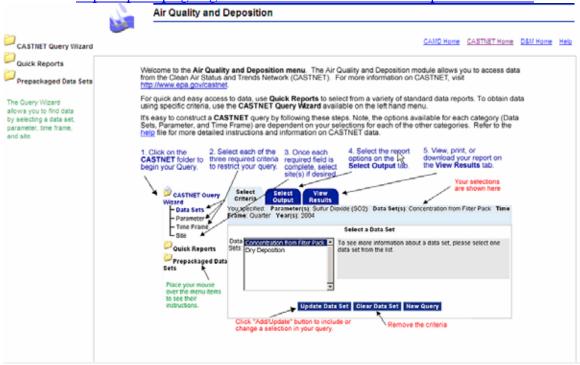


Figure 3-2. Trends in total nitrogen and total sulfur deposition in Shenandoah NP (from CASTNet at <a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>); NO3=nitrate; HNO3=nitric acid; NH4=ammonium; SO2=sulfur dioxide; SO4=sulfate.

Data (dry or total deposition, dry particle concentration, meteorology, ozone) can also be downloaded from CASTNet for further analysis. To download total deposition data for Shenandoah, for example:

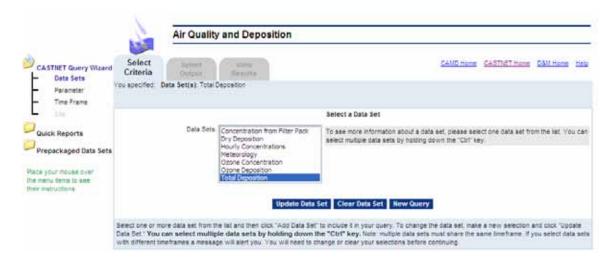
From the CASTNet site (<a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a>), select "Data." You will be directed to <a href="http://cfpub.epa.gov/gdm/index.cfm?fuseaction=aciddeposition.wizard/">http://cfpub.epa.gov/gdm/index.cfm?fuseaction=aciddeposition.wizard/</a>:



Select "CASTNet Query Wizard" from items on left of page.



From Data Set list, choose "Total Deposition"; select "Add Data Set"



On left of page select "Parameter"; on drop-down list, select "Total Nitrogen" and "Total Sulfur"; select "Add Parameters"



On left of page select "Time Frame", select "Year", then select 1995-2004.



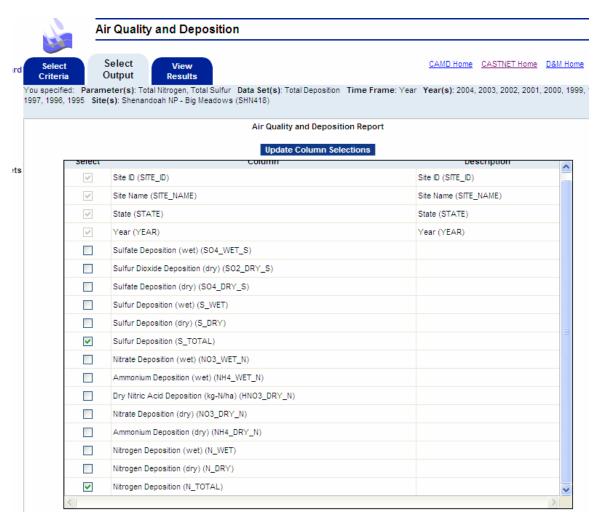
On left of page select "Site"; under State choose "Virginia", select "Find Sites" From "Matching Sites" select Shenandoah; move it to "Selected Sites"; then, "Add Sites"



Your specified parameters should now be total nitrogen, total sulfur, total deposition, 1995-2004, Shenandoah:



Select tab "Select Output" and uncheck all items except Sulfur Deposition (S\_TOTAL) and Nitrogen Deposition (N\_TOTAL); "Update Column Selections"



#### Select "View Results" tab.

DOWNLOAD ALL DATA using the buttons below (download is limited to 20,000 rows).  SORT results by clicking on a column name (once=ascending, twice=descending).								
	New Query Dov	vnload All Data	Report De	finitions View Column C	Codes			
(10 records in 1 page of 10 records)								
Site ID (SITE_ID)	Site Name (SITE_NAME)	State (STATE)	Year (YEAR)	Sulfur Deposition (S_TOTAL)	Nitrogen Deposition (N_TOTAL)			
SHN418	Shenandoah NP - Big Meadows	VA	1995	10.72	9.62			
SHN418	Shenandoah NP - Big Meadows	VA	1996	<sup>15</sup> 11.63	9.77			
SHN418	Shenandoah NP - Big Meadows	VA	1997	9.88	8.12			
SHN418	Shenandoah NP - Big Meadows	VA	1998	11.34	8.99			
SHN418	Shenandoah NP - Big Meadows	VA	1999	10.12	8.31			
SHN418	Shenandoah NP - Big Meadows	VA	2000					
SHN418	Shenandoah NP - Big Meadows	VA	2001	8.8	7.61			
SHN418	Shenandoah NP - Big Meadows	VA	2002	9.23	8.02			
SHN418	Shenandoah NP - Big Meadows	VA	2003					
SHN418	Shenandoah NP - Big Meadows	VA	2004	9.81	8.06			

Dry particle concentration data can also be downloaded from the CASTNet Query Wizard by selecting "Concentration from Filter Pack." Data from multiple sites can be downloaded for comparison, or national maps of deposition or dry particle or gas concentrations can be used to compare Shenandoah's data to other sites. Maps are available at <a href="http://www.epa.gov/castnet/mapindex.html">http://www.epa.gov/castnet/mapindex.html</a>; higher quality maps are available from the CASTNet Annual Reports. For example, figures 3-3 through 3-6, from the CASTNet Annual Report 2004 (<a href="http://www.epa.gov/castnet/library.html">http://www.epa.gov/castnet/library.html</a>) show national maps with interpolations of dry particle (nitrate, ammonium, and sulfate) or gas (sulfur dioxide) concentrations in micrograms per cubic meter for 2004.

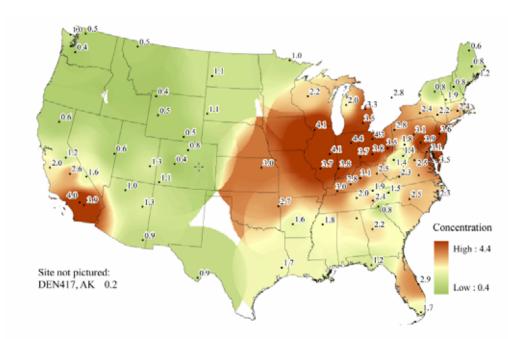


Figure 3-3. Annual mean dry nitrate concentrations in micrograms per cubic meter for 2004 (CASTNet Annual Report 2004).

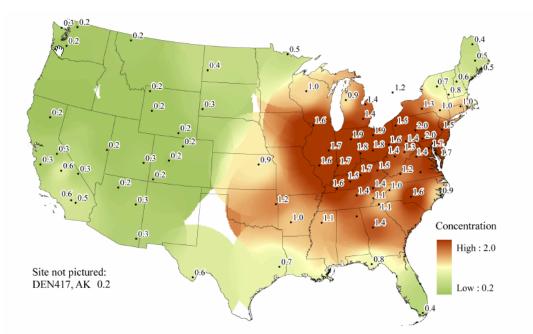


Figure 3-4. Annual mean dry ammonium concentrations in micrograms per cubic meter for 2004 (CASTNet Annual Report 2004).

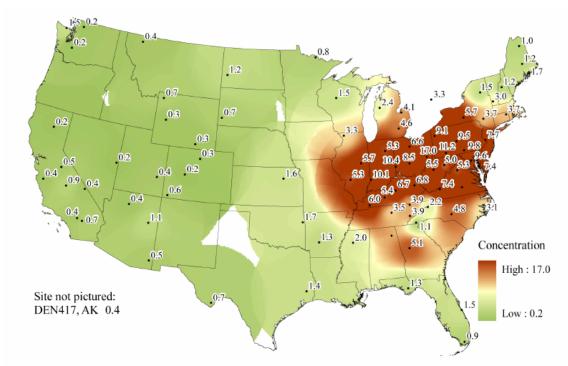


Figure 3-5. Annual mean dry sulfur dioxide concentrations in micrograms per cubic meter for 2004 (CASTNet Annual Report 2004).

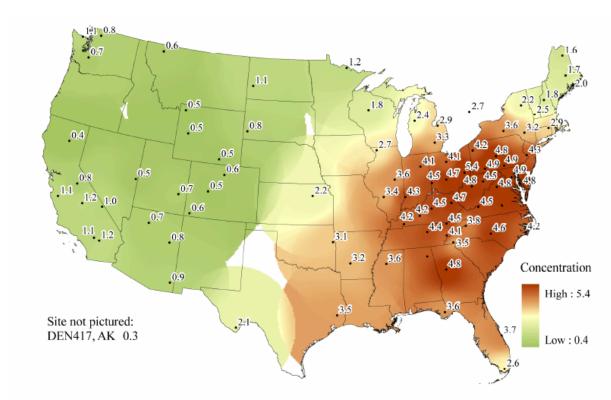


Figure 3-6. Annual mean dry sulfate concentrations in micrograms per cubic meter for 2004 (CASTNet Annual Report 2004).

These maps show that Shenandoah NP experiences relatively high concentrations of nitrate, ammonium, sulfur dioxide, and sulfate, typical of eastern sites and reflecting high vehicle density, power production, and agricultural activity in the region. Across all sampling sites, annual mean nitrate concentrations ranged from 0.4-4.4 micrograms per cubic meter ( $\mu g/m^3$ ) in 2004, with "hotspots" in the Midwest, East, and southern California; at Shenandoah, mean nitrate was 2.5  $\mu g/m^3$ . Nitrate results primarily from nitrogen oxides emissions from vehicles and power plants. Annual mean ammonium concentrations ranged nationally in 2004 from 0.2-2.0  $\mu g/m^3$ , with hotspots in the East and Midwest; at Shenandoah, mean ammonium was 1.4  $\mu g/m^3$ . Ammonium results primarily from crop and livestock production. As noted in Section 2.0, CASTNet does not measure gaseous ammonia. A map showing gaseous ammonia deposition might be expected to look somewhat different from the map of particulate ammonium deposition, with hotspots shifted somewhat to the West, to reflect the large agricultural contributions in the Midwest.

Annual mean sulfur dioxide concentrations nationwide in 2004 ranged from 0.2-17.0  $\mu g/m^3$  with hotspots in the Ohio River Valley and East; at Shenandoah, mean sulfur dioxide was 5.3  $\mu g/m^3$ . Sulfur dioxide is emitted primarily by coal-burning power plants. Annual mean sulfate concentrations in 2004 ranged nationally from 0.4-5.4  $\mu g/m^3$ , with hotspots throughout the East; at Shenandoah, mean sulfate was 4.8  $\mu g/m^3$ . Sulfate is formed from sulfur dioxide emissions as they are carried downwind and transformed in the atmosphere.

The concentration maps indicate that Shenandoah NP has some of the highest concentrations of pollutants in the country. However, aquatic and terrestrial ecosystems are affected not so much by pollutant particles in the air as by pollutants deposited on water or land. Figures 3-7 and 3-8 show deposition, in kilograms per hectare per year (kg/ha/yr) of dry nitrogen and sulfur for 2004.

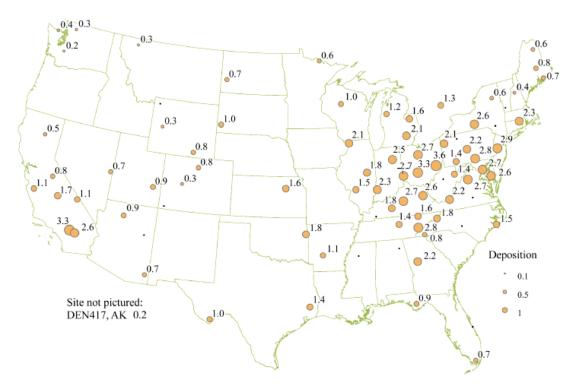


Figure 3-7. Dry nitrogen deposition in kilograms per hectare for 2004 (CASTNet Annual Report 2004).

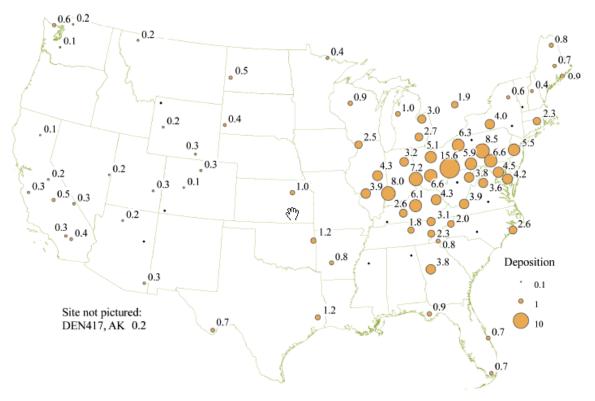


Figure 3-8. Dry sulfur deposition in kilograms per hectare for 2004 (CASTNet Annual Report 2004).

Dry deposition rates of nitrogen and sulfur are relatively high at Shenandoah NP. Dry deposition of nitrogen ranged nationally in 2004 from 0.2-3.6 kg/ha/yr, with 2.7 kg/ha/yr at Shenandoah NP. Dry deposition of sulfur ranged nationally from 0.1-15.6 kg/ha/yr in 2004, with 3.6 kg/ha/yr at Shenandoah NP.

Note that the dry deposition values are not interpolated, as are the concentration values. Dry deposition estimates are site-specific; as noted in Section 2.0, concentration measurements are combined with deposition velocities (derived from the Multi-Layer Model - MLM) to estimate dry deposition of gaseous and aerosol pollutants at specific sites. CASTNet does not interpolate dry deposition because deposition velocities can vary significantly from one location to another due to variations in vegetation and meteorology, whereas concentrations of dry particles tend to be somewhat evenly dispersed. For this reason, wet and dry deposition measurements should be co-located so that total deposition can reasonably be estimated.

Figures 1-2 and 1-3 from Section 1.0 of this report are maps of total sulfur and nitrogen deposition from the 2004 CASTNet Annual Report; these maps combine both dry deposition data from CASTNet and wet deposition data from NADP/NTN for estimates of total deposition for sites with both measurements. Total sulfur deposition ranged from 0.5-27.2 kg/ha/yr, with 9.8 kg/ha/yr at Shenandoah NP. Total nitrogen deposition ranged from 1.1-10.1 kg/ha/yr, with 7.9 kg/ha/yr. These rates are greatly elevated over natural background rates of approximately 0.5 kg/ha/yr for total nitrogen and 0.5 kg/ha/yr for total sulfur.

The Shenandoah Air Quality Assessment 2003 at <a href="http://www.nps.gov/shen/air\_quality.htm">http://www.nps.gov/shen/air\_quality.htm</a> discusses the impacts that elevated deposition has caused in the park, including acidified streams and reduced fish populations. Information on ecosystem sensitivity to deposition in other parks can be found in the NPS-ARD Air Resources Information System (ARIS) at <a href="http://www2.nature.nps.gov/air/Permits/ARIS/index.cfm">http://www2.nature.nps.gov/air/Permits/ARIS/index.cfm</a>. Some parks have low acid-buffering capacity of waters or soils and may be acidified by nitrogen or sulfur deposition. Other parks may have aquatic or terrestrial ecosystems that are nitrogen-limited; these ecosystems may be unfavorably altered by nitrogen deposition.

#### 4.0 RELEVANT WEBSITES

CASTNet: <a href="http://www.epa.gov/castnet/">http://www.epa.gov/castnet/</a> NADP: <a href="http://nadp.sws.uiuc.edu/">http://nadp.sws.uiuc.edu/</a>

NPS Air Resources Division: <a href="http://www2.nature.nps.gov/air/">http://www2.nature.nps.gov/air/</a>

NPS ARIS: http://www2.nature.nps.gov/air/Permits/ARIS/index.cfm